

# Limited robustness of edge magnetism in zigzag graphene nanoribbons with electrodes

**S. Krompiewski**

Institute of Molecular Physics, Polish Academy of Sciences, ul. M. Smoluchowskiego 17, 60179 Poznań, Poland

**Abstract.**

It is shown that apart from well-known factors, like temperature, substrate, and edge reconstruction effects, also the presence of external contacts is destructive for the formation of magnetic moments at the edges of graphene nanoribbons. The edge magnetism gradually decreases when graphene/electrode interfaces become more and more transparent for electrons. In addition to the graphene/electrode coupling strength, also the aspect ratio parameter, i.e. a width/length ratio of the graphene nanoribbon, is crucial for the suppression of edge magnetism.

The present theory uses a tight-binding method, based on the mean-field Hubbard Hamiltonian for  $\pi$  electrons, and the Green's function technique within the Landauer-Büttiker approach.

PACS numbers: 81.05.ue, 75.47.De, 73.23.Ad

## 1. Introduction

The problem of edge states in carbon nanoribbons is an important issue which has been intensively studied for almost 20 years now, i.e since the edge states were first theoretically predicted [1]. Experimental confirmations of this concept came a few years later ([2] and [3]). Since then, a lot of theoretical papers have been devoted to the edge state problem. Magnetic edge states were examined, e.g. in Refs [4]- [7], where fundamental for spintronics phenomena - such as spin transport, giant magnetoresistance and Coulomb blockade effects - were studied. Recently the problem has been given an additional impetus due to new challenges related with a rich class of graphene-like materials. Some of them, in contrast to graphene, possess a significant spin-orbit coupling and are of interest as potential quantum spin Hall systems and/or topological insulators ([8]-[10]).

The edge states become of particular importance in nanostructures because then a great fraction of atoms lies at the edges, what strongly influences electronic - and thereby chemical, electrical and probably magnetic - properties. The latter will be focused on in this study. It is well-known that at zigzag type fragments of graphene's edges the electronic states are of localized nature, with the exponentially decaying amplitude as the interior is approached. These states have very flat energy spectra in the vicinity of the charge neutrality point, hence their density of states may be high enough to satisfy the so-called Stoner criterion for the appearance of magnetism. The problem is still open, and there is a lively debate on it. On the one hand there are sceptic opinions, stressing that a number of factors can destroy the edge state magnetism, including the temperature, reconstruction (or closure) of edge atoms, as well as passivation thereof [11]. On the other hand however there are already experimental results obtained by STM and STS (scanning tunneling microscopy and spectroscopy) methods which provide results supporting the view that spin-degeneracy of edge states may be lifted [12]. Complexity of the problem has recently been convincingly presented in Ref. [13], where it is pointed out that whether or not edge magnetic moments can exist depends also on the substrate material they are in contact with.

In this study, it is shown that  $\pi$ -electron edge states can even be affected if the edge atoms are relatively far away (up to a few tens of angstroms) from the non-local disturbance due to contacts. This is in contrast to the hitherto known situations corresponding to the edge reconstruction [14], edge atom closure and hydrogenation [11], as well as the temperature and substrate effects [13]. Indeed, it results from the present findings that carbon edge atoms distant from the external electrodes may lose their magnetic moments, unless the GNR is weakly coupled to the contacts. This means that the promising concepts to use GNRs as spintronic devices (see [15, 16, 17]), might be realized provided that electrodes are properly selected. In particular contacts ensuring the formation of high resistive interfaces with the graphene nanoribbons (GNR) - possibly tunneling junctions - should be applied.

## 2. Methodology and Modeling

The present approach is based on the tight-binding Hubbard model in the mean-field approximation.

$$H = - \sum_{i,j,\sigma} t_{i,j} |i, \sigma\rangle \langle \sigma, j| + \frac{1}{2} \sum_{i,\sigma} \Delta_{i,\sigma} |i, \sigma\rangle \langle \sigma, i|, \quad (1)$$

$$\Delta_{i,\sigma} = U(n_{i,\sigma} - n_{i,-\sigma}), \quad (2)$$

with the nearest neighbor hopping parameter  $t = t_{i,j}$ , intra-atomic Coulomb repulsion  $U$  and the  $\sigma$ -spin occupation number  $n_{i,\sigma}$  at the lattice site  $i$ . Well established values of the hopping parameter for graphene ( $t_G$ ) range between 2.7 eV and 3 eV. As concerns the  $U$  parameter, it is still under debate (*cf.*  $U$  equal to 0.5 eV in [18] and  $U=1.2 t_G$  in [17]). In this paper a moderate value of  $U/t_G = 0.6$  is used.

On the one hand the occupation number in the case of non-contacted (free standing) GNRs can be determined, after having diagonalized the Hamiltonian (1),  $(H - E)|u_E\rangle = 0$ , as

$$n_{i,\sigma} = \sum_{E < E_F} |u_E^{i,\sigma}|^2 \quad (3)$$

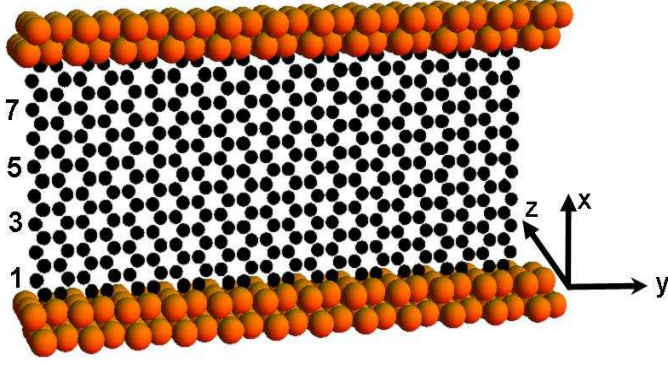
On the other hand in the presence of external contacts, the occupation number can be found, applying the Green's function technique, in terms of self-energies  $\Sigma_1$  and  $\Sigma_2$  for source and drain electrodes, respectively. The corresponding equations read:

$$\begin{aligned} n_i &= -\frac{1}{\pi} \int_{-\infty}^{E_F} dE \operatorname{Im} \mathcal{G}_{i,i}(E), \\ \mathcal{G} &= (\hat{1}E - H - \Sigma_1 - \Sigma_2)^{-1}, \\ \Sigma_{1,2} &= \hat{t}_c g_{1,2} \hat{t}_c^\dagger. \end{aligned} \quad (4)$$

Above, the self-energies are defined as products of the electrode/GNR hopping parameter matrices ( $\hat{t}_c$ ) and corresponding surface Green's functions ( $g$ ) of the electrodes. The contacts are modeled by surface Green's functions of a close packed semi-infinite face centered cubic lattice, fcc(111), which for the single-band model used here are known analytically (see [19, 20, 21] for details). No periodic boundary conditions have been employed.

Now it is possible to compute the following physical properties of interest here, *i.e.* local magnetic moments ( $m$ ), conductance ( $G$ ), transmission ( $T$ ) and shot noise Fano factor:

$$\begin{aligned} m &= n_{i,\uparrow} - n_{i,\downarrow}, \\ G &= \frac{e^2}{h} \operatorname{Tr}(T), \quad T = \Gamma_1 \mathcal{G} \Gamma_2 \mathcal{G}^\dagger, \end{aligned}$$



**Figure 1.** (Color online) Perspective view of the 3-dimensional setup composed of the (11, 9) GNR (small spheres in the x-y plane), and the electrodes infinite in the y-z plane, and semi-infinite in the x direction (only atoms close to the interface - larger spheres - are shown). Carbon atoms are enumerated column-wise, from the bottom upwards.

$$\begin{aligned}\Gamma_{1,2} &= i(\Sigma_{1,2} - \Sigma_{1,2}^\dagger), \\ F &= 1 - \text{Tr}(T^2)/\text{Tr}(T).\end{aligned}\tag{5}$$

A representative setup considered here is presented in Fig. 1.

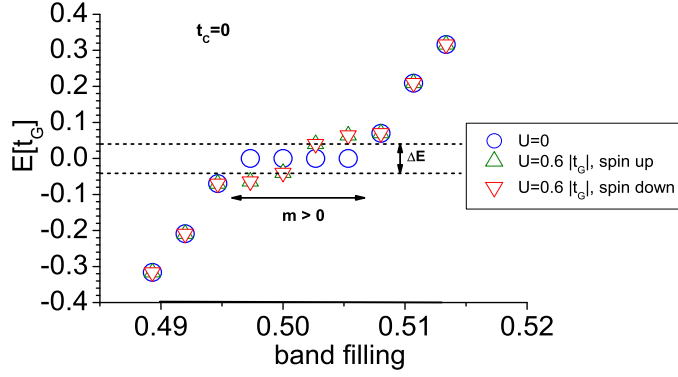
The GNRs are characterized by two numbers ( $N_a$ ,  $N_z$ ) related with the number of unit cells in the armchair and zigzag directions, respectively. Thus, the number of carbon atoms along the edge (interface) boundary is equal to  $N_z-1$  ( $2 N_a$ ). The undercoordinated edge atoms are assumed to be passivated by hydrogen, so there are no  $\sigma$ -type dangling bonds.

### 3. Results

The most important question we focus on is the influence of the contacts on the edge magnetism, i.e. magnetic moments of the carbon atoms along the outermost zigzag lines. In order to elucidate this point a number of GNRs has been studied. It turns out that apart from the obvious relevance of the interface coupling, modeled by a hopping integral strength between GNR/contact atoms  $t_c$ , also the aspect ratio of the GNR defined as  $A=\text{width}/\text{length}$  is of importance. So in the following, edge atom magnetic profiles are presented both for non-contacted ( $t_c = 0$ ) as well as contacted GNRs of various  $A$  parameters.

A typical energy spectrum around the charge neutrality point for a GNR is presented in Fig. 2.

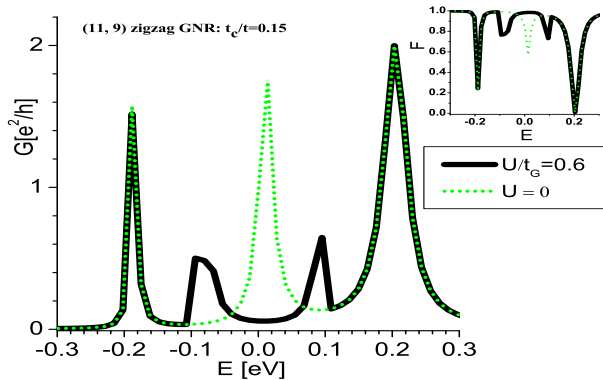
It is consistent with the next figure (Fig. 3) representing the conductance spectrum, with contacts relatively weakly coupled to the GNR ( $t_c/t_G = 0.15$ ).



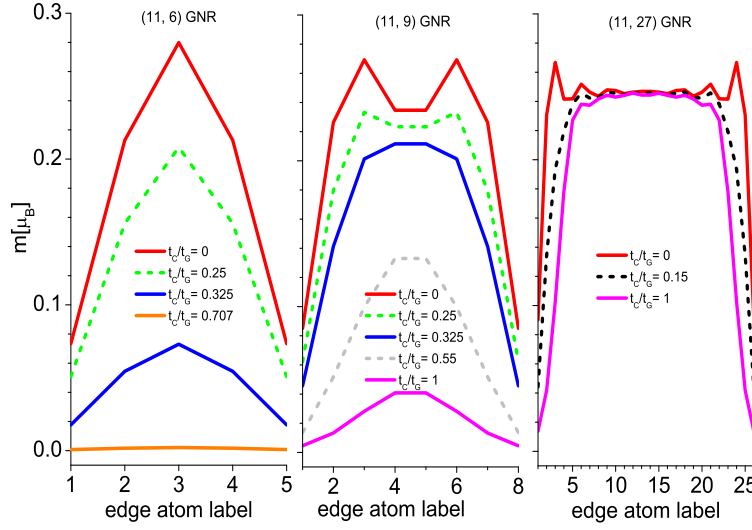
**Figure 2.** (Color online) Energy spectrum of the (11, 9) free standing GNR close to the half band filling for non-magnetic and magnetic cases (sphere and triangle markers, respectively). Away from the charge neutrality point, all the markers coincide, meaning disappearance of the magnetism.

The presence of the contacts results in a slight shift of the Fermi energy with respect to the unperturbed case of  $E_F = 0$ . In order to gain a deeper insight into the doping problem, the magnetic profiles along the zigzag edges have been first determined for the Fermi energy  $E_F = 0$  (as for the free standing GNR with  $t_c = 0$ ), Fig. 4, and next for  $E_F$  corresponding to the charge neutrality point (CNP).

Although, in general, unintentional doping coming from electrodes depends on the difference in respective work functions (WFs) of the electrodes and the GNR, it turns out that the p-type doping is expected in the case of high-WF metals that couple weakly to GNR (e.g. Au [22, 13]). As shown in Fig. 5 the present model fits qualitatively to this scenario.

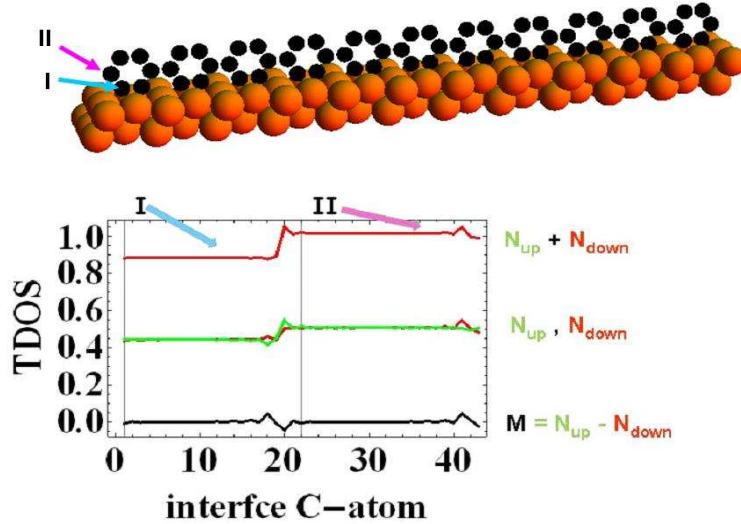


**Figure 3.** (Color online) Conductance and the shot noise Fano factor for the (11, 9) GNR. Close to  $E=0$  the plots for finite  $U$  and  $U=0$  differ greatly, otherwise they coincide with each other.

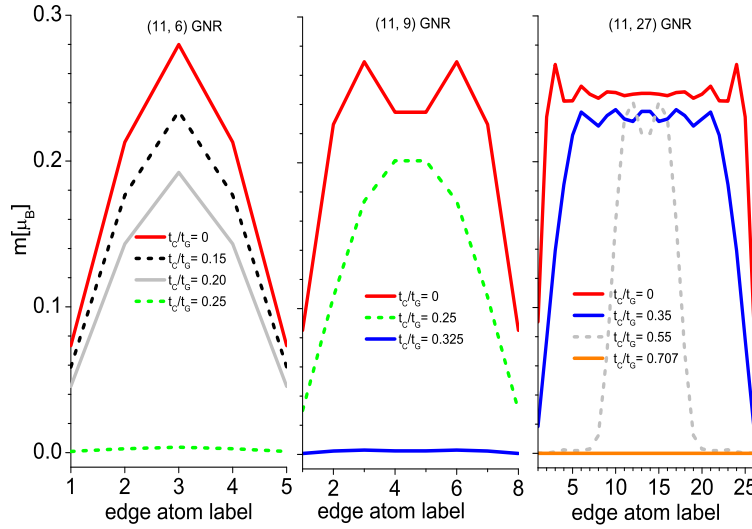


**Figure 4.** (Color online) Edge magnetization profiles for 3 different aspect ratio GNRs, indicated  $t_c$  parameters, and  $E_F = 0$ . Magnetic moments at the other zigzag edge are oppositely oriented.

In Fig. 6, in turn, the  $E_F$  correspond to the actual CNPs. It is readily seen that both in Fig. 4 and Fig. 6 the increasing strength of the  $t_c$  coupling suppresses edge magnetic moments. The effect is the most pronounced when the setups are wide and short (big A). However, in the case of  $E_F = \text{CNP}$  it is possible to quench completely all the magnetic moments even for the (11, 27) GNR (with the aspect ratio clearly less than



**Figure 5.** (Color online) The profiles of the number of electrons in the (11, 27) GNR with  $t_c/t_G = 0.15$ . Region I corresponds to the interface carbon atom line (nearest to the contact), whereas the region II is the next nearest line of atoms.  $N_{up}$  ( $N_{down}$ ) stands for the number of spin up (down) electrons. Charge depletion in the region I is readily seen.



**Figure 6.** (Color online) As Fig. 4 but for Fermi energies equal to the charge neutrality points.

one), provided that  $t_c \sim 0.7t_G$ .

The present findings agree qualitatively with Ref. [13], where edge states and edge magnetism in graphene nanoribbons were studied by means of an *ab initio* method. Although those studies concerned the substrate effects instead of the contact ones, they led to conclusions which bear some resemblance to the present ones. First of all, the edge magnetism was shown there to disappear in the case of closed-packed surfaces of the substrates with a strong graphene/substrate coupling (Cu and Ag), in contrast to the Au substrate of weaker coupling. These metallic substrate effects may be related to the present results in terms of our  $t_c$  parameter, which for the Cu and Ag substrates is clearly higher than for the Au one, due to differences in the respective carbon/substrate-atom distances. Remarkably, typical edge magnetic moments (of roughly 0.2 - 0.3  $\mu_B$  per C atom) found here do also agree with those reported in Ref. [13]. So, despite the fact that the present approach is qualitative rather than quantitative, it provides some indirect insight into the chemical nature of the contacts. Indeed the phenomenological parameters  $t_c$ , which in fact depend on orbital hybridization and a bond length at the interface, can be related to material specific *ab initio* results.

#### 4. Conclusions

Summarizing, in accordance with common knowledge it has been confirmed here that non-contacted (free standing) GNRs reveal edge magnetism in the zigzag outermost carbon atoms. Remarkably, the magnitude of the edge magnetic moments is sensitive to the GNR/contact coupling strength and the separation of the given edge atom from the interface. In the case of high aspect ratio GNRs the zigzag edge magnetic moments may be severely reduced or even completely quenched. The present findings concerning the

conductance and the Fano factor indicate that magnetic moments can also be suppressed by applying a gate voltage that brings the system to the state far enough away from the charge neutrality point.

## 5. Acknowledgments

This project was supported by the Polish National Science Centre from funds awarded through the decision No. DEC-2013/10/M/ST3/00488.

## References

- [1] Nakada K, Fujita M, Dresselhaus G and Dresselhaus M S 1996 *Phys. Rev. B* **54** 17954
- [2] Klusek Z, Waqar Z, Denisov E, Kompaniets T, Makarenko I, Titkov A and Bhatti A 2000 *Appl. Surf. Sci.* **161** 508
- [3] Kobayashi Y, Fukui K-I, Enoki T, Kusakabe K and Kaburagi Y 2005 *Phys. Rev. B* **71** 193406
- [4] Wimmer M, Adagideli I, Berber S, Tomanek D and Richter K 2008 *Phys. Rev. Lett.* **100** 177207
- [5] Munoz-Rojas F, Fernandez-Rossier J and Palacios J J 2009 *Phys. Rev. Lett.* **102** 136810
- [6] Weymann I, Barnaś J and Krompiewski S 2012 *Phys. Rev. B* **85** 205306
- [7] Gosálbez-Martínez D, Soriano D, Palacios J J and Fernandez-Rossier J 2012 *Sol. Stat. Comm.* **152** 1469
- [8] Xu Ch, Luo G, Liu Q, Zheng J, Zhang Z, Nagase S, Gao Z, and Lu J, 2012 *Nanoscale* **4** 3111
- [9] Zborecki K, M. Wierzbicki M, Barnaś J, and Swirkowicz R 2013 *Phys. Rev. B* **88** 115404
- [10] Rachel S and Ezawa M 2014 *Phys. Rev. B* **89** 195303
- [11] Kunstmann J, Özdoğan C, Quandt A and Fehske H 2011 *Phys. Rev. B* **83** 045414
- [12] Tao C, Jiao L, Yazyev O V, Chen Y -C, Feng J, Zhang X, Capaz R B, Tour J M, Zettl A, Louie S G, Dai H and Crommie M F 2011 *Nat. Phys.* **7** 616
- [13] Li Y, Zhang W, Morgenstern M and Mazzarello R 2013 *Phys. Rev. Lett.* **110** 216804
- [14] Koskinen P, Malola S and Häkkinen H 2009 *Phys. Rev. B* **80** 073401
- [15] Son Y -W, Cohen M L and Louie S G 2006 *Nature (London)* **444** 347
- [16] Kim W Y and Kim K S 2008 *Nat. Nanotechnol.* **3** 408
- [17] Yazyev O V 2010 *Rep. Progr. Phys.* **73** 056501
- [18] Nair R R, Tsai I -L, Sepioni M, Lehtinen O, Keinonen J, Krasheninnikov A V, Castro Neto A H, Katsnelson M I, Geim A K and Grigorieva I V 2013 *Nat. Commun.* **4** 2010
- [19] Todorov T N, G. Briggs G A D and Sutton A P 1993 *J. Phys.: Condens. Matter* **5** 2389
- [20] Krompiewski S 2009 *Phys. Rev. B* **80** 075433
- [21] Krompiewski S 2012 *Nanotechnology* **23** 135203
- [22] Giovannetti G, Khomyakov P A, Brocks G, Karpan V M, van den Brink J and Kelly P J 2008 *Phys. Rev. Lett.* **101** 026803